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(71) Applicant: MATSUSHITA ELECTRONICS
CORPORATION
1006, Ohaza Kadoma
Kadoma-shi, Osaka 571(JP)

(72) Inventor: Okuyama, Kojiro
2-6-1, Inaba Nishi,
Ikaruga-cho
Ikoma-gun, Nara, 636-01(JP)
Inventor: Yokotani, Yoichiro
8-C-508, Satsukigaoka higashi
Suita-shi, Osaka, 565(JP)
Inventor: Kugimiya, Koichi
2-1-32, Chokoji minami
Toyonaka-shi, Osaka, 560(JP)

(74) Representative: VOSSIUS & PARTNER
Postfach 86 07 67
D-81634 München (DE)

(54) Dielectric ceramic compositions and dielectric resonators.

(57) The invention provides a dielectric ceramic including as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of {Mg, Co, Zn, Ni and Mn} and at least one component selected from the group (B) consisting of {Nb and Ta} and a TE_{01δ}-mode dielectric resonator including the dielectric ceramic, and also the invention provides a dielectric ceramic composition expressed by Formula (a):



wherein A denotes at least one component selected from the group (A) consisting of {Mg, Co, Zn, Ni and Mn},
x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.20 to 0.60 and 0.01 to 0.70, respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula (α)}$$

and w denotes a value of 0 to 1.50, and a TE_{01δ}-mode dielectric resonator in which using the dielectric ceramic.

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This invention relates to dielectric ceramics and dielectric resonators for use in such high-frequency ranges as microwave and millimeter-wave frequencies.

Recently, dielectric ceramics have been widely used in dielectric resonators and filters in microwave and millimeter-wave frequencies at wavelengths of several centimeters or less (hereinafter referred to as microwave in general). It is required that a dielectric material for use in such applications have a high unloaded Q (Qu) value and dielectric constant ϵ_r , and that the temperature coefficient at resonant frequency τ_f be variable as desired.

Various materials appropriate for use in such applications have been conventionally reported, among which ZrTiO₄ ceramics are included. Also included in such materials are ZrO₂-SnO₂-TiO₂ ceramics, the ZrO₂-SnO₂-TiO₂-MgO ceramic suggested in Japanese Laid-Open Patent No. 62-132769 and the ZrO₂-SnO₂-TiO₂-CoO-Nb₂O₅ ceramic in No. 2-192460 are known, for example.

However, although ZrTiO₄ ceramics have a high dielectric constant of 45, the temperature coefficient at resonant frequency is high in the positive side at 54 ppm/°C, and the temperature coefficient is significantly varied by the heating history during sintering. ZrO₂-SnO₂-TiO₂ ceramic system achieved a low temperature coefficient at resonant frequency nearly zero, but the heating history problems didn't solved satisfactory.

In addition, conventional materials have such problems that the dielectric constant and unloaded Q value are low, and that the temperature coefficient at resonant frequency cannot be varied as desired.

Moreover, although the product of resonant frequency (f) × Qu value is generally regarded as being constant in a given material, when f is lowered (that is, an element is enlarged), actually, the product fQu is reduced (decreased). Therefore, there is a strong demand for a dielectric element for microwave applications such as a dielectric resonator for a base station of mobile radio communication system used in a relatively low frequency range with a higher unloaded Q value. Furthermore, because dielectric resonators used in the relatively low frequency ranges are very bulky, reduction in size is highly demanded.

The object of the present invention is to provide ZrTiO₄ and ZrO₂-SnO₂-TiO₂ dielectric ceramics with less variation of temperature coefficient at their resonant frequency due to heating history during sintering.

It is another object of the invention to provide dielectric ceramics that have a high unloaded Q value and high dielectric constant, and have a temperature coefficient at resonant frequency which is variable as desired.

It is still another object of the invention to provide TE_{01δ}-mode dielectric resonators having a high unloaded Q value in a frequency range of 0.8 to 5 GHz with a compact size.

The subject of the invention is to achieve one of these objects or to achieve more than two objects at the same time.

The invention relates to a dielectric ceramic comprising as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.

The invention also relates to a dielectric ceramic composition expressed by Formula (a):



wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.20 to 0.60 and 0.01 to 0.70, respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula (α)}$$

and w denotes a value of 0 to 1.50.

The invention also relates to a dielectric ceramic composition expressed by Formula (b):



wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.10 to 0.60 and 0.01 to 0.80, respectively, and have the relation represented by Formula (α):

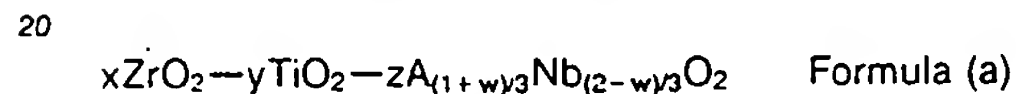
$$x + y + z = 1 \quad \text{Formula (α)}$$

and w denotes a value of 0 to 1.00.

The invention also relates to a dielectric ceramic in which the main component comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, or the main component crystallographically comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.

The invention also relates to a dielectric ceramic in which the main component comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, or the main component crystallographically comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, wherein the molar fraction ratio of the total amount of the group (A) components to the total amount of the group (B) components ranges from 0.5 to 1.0.

The invention also relates to a $\text{TE}_{01\delta}$ -mode dielectric resonator comprising a dielectric ceramic which comprises as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta. The invention also relates to a $\text{TE}_{01\delta}$ -mode dielectric resonator comprising a dielectric ceramic expressed by Formula (a):



wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.20 to 0.60 and 0.01 to 0.70, respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula } (\alpha)$$

and w denotes a value of 0 to 1.50.

The invention also relates to a $\text{TE}_{01\delta}$ -mode dielectric resonator comprising a dielectric ceramic expressed by Formula (b):



wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.10 to 0.60 and 0.01 to 0.80, respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula } (\alpha)$$

and w denotes a value of 0 to 1.00.

The invention also relates to a $\text{TE}_{01\delta}$ -mode dielectric resonator in which the main component comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, or the main component crystallographically comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.

The invention also relates to a $\text{TE}_{01\delta}$ -mode dielectric resonator in which the main component comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, or the main component crystallographically comprises a ZrTiO_4 phase substituted with at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta, wherein the molar fraction ratio of the total amount of the group (A) components to the total amount of the group (B) components ranges from 0.5 to 1.0.

DETAILED DESCRIPTION OF THE INVENTION

Any compound such as oxide, carbonate, hydroxide, alkoxide of the component elements described above may be used as an initial material of the dielectric ceramic according to the present invention.

5 As blending methods of powdery raw materials, wet blending for mixing the materials with water or organic solvent in a ball mill and dry blending for mixing them by a mixer or a ball mill, etc. without using any solvent are generally known, and any of these methods may be employed. Alternatively, the alkoxide method and coprecipitation method may be used depending on the initial materials. This means that various known methods applicable to manufacture of dielectric ceramics can be employed. Because the process is
10 thus comparatively uncomplicated, and a homogeneous mixture can be easily obtained, it is desirable to employ the wet blending method for mixing them in a ball mill by using a solvent, and a dispersing agent may be additionally used for increasing the dispersing property of powders, or pH adjustment may be performed.

Although calcination of the mixture is not required, the sintering time can be reduced by calcination.
15 Although the calcination temperature depends on the particular compositions, it is generally in the order of 2 to 8 hrs at about 800 to 1250 °C.

As milling method of the calcined material or mixture, any such method of using a ball mill, high-speed rotor mill, media agitating mill and jet mill may be employed.

For molding, press molding is generally carried out to obtain a desired shape. Although not specifically
20 limited, pressure used in the press molding is generally in a range of approximately 0.5 to 1.5 ton/cm².

Although the sintering is not specifically limited, as it depends on the particular compositions and dimensions of the moldings, it is generally desirable to perform firing at a temperature of approximately 400 to 700 °C for about 1 to 100 hrs in order to remove binders, then, at approximately 1300 to 1650 °C for about 1 to 10 hrs.

25

Example 1

As initial materials, ZrO₂, TiO₂, MgO, CoO, ZnO, NiO, Nb₂O₅ and MnCO₃ of high chemical purity were used, weighed so as to make a predetermined compositions as shown in Table 1 at the end of this
30 specification, and wet-blended with ethanol by using a ball mill. The volume ratio between the powders and ethanol was approximately 2:3. The mixture was removed from the ball mill, dried, and calcined for 2 hours at 1000 °C in the air. The calcination product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powders were mixed with 8% by weight of polyvinyl alcohol solution of 6% in concentration added thereto as a binder, homogenized, and granulated by sieving
35 through 32 mesh screen. The granulated powders were molded into a disk of 7 mm in diameter and approximately 3 mm in thickness by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm². The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 600 °C for 4 hrs to remove binders, then retained in the air at 1500 °C for 24 hrs for sintering, and quenched (taken out of a furnace and air-cooled) or slowly cooled (at a cooling rate of 20 °C/hr) thereafter,
40 and dielectric ceramics were obtained.

The resonant frequency was obtained from measurement by the dielectric rod resonator method. The temperature coefficient at resonant frequency τ_f was obtained in a range between -25 and 85 °C.

Compositions of dielectric ceramics thus produced are shown in Table 1, and cooling conditions after sintering and temperature coefficients at resonant frequency (ppm/°C) in Table 2. In Table 1 and Table 2,
45 those with an asterisk are comparison examples.

As recognized from the results shown in Table 2, in dielectric ceramics of sample Nos. 3 to 10 variation of temperature coefficient at resonant frequency due to the heating history during sintering of ZrTiO₄ and ZrO₂-SnO₂-TiO₂ ceramics are reduced. In addition, similar effects were confirmed in dielectric ceramics with 0.5 mol% of at least one compound of Al₂O₃, SiO₂, BaCO₃, SrCO₃, La₂O₃ and Sm₂O₃ added to those
50 of sample Nos. 3 to 10. Other components may be added as far as the objects of the invention are not adversely affected.

According to the first aspect of the invention, variation of temperature coefficient at resonant frequency due to the heating history during sintering of ZrTiO₄ and ZrO₂-SnO₂-TiO₂ ceramics can be reduced.

55 Example 2

As initial materials, ZrO₂, TiO₂, MgO, CoO, ZnO, NiO, MnCO₃ and Nb₂O₅ of high chemical purity were used, weighed so as to make a predetermined composition as shown in Table 3, and wet-blended with

ethanol by using a ball mill. The volume ratio between the powders and ethanol was approximately 2:3. The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hrs at a temperature of 800 to 1250 °C in the air. The calcination product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powders were mixed with 8% by weight of polyvinyl alcohol solution of 6% in concentration added thereto as a binder, homogenized, and granulated by sieving them through 32 mesh screen. The granulated powders were molded into a disk of 7 mm in diameter and approximately 3 mm in thickness by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm². The molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 400 to 700 °C for 4 to 8 hrs to remove binders, and retained thereafter in the air at a temperature of 1300 to 1650 °C for one to 100 hrs for sintering, and dielectric ceramics were obtained. The resonant frequency, unloaded Q (Q_u) value and dielectric constant ϵ , were obtained by measurement with the dielectric rod resonator method. The temperature coefficient at resonant frequency τ , was obtained in a range between -25 and 85 °C. The resonant frequency was within a range of 5 to 10 GHz.

The dielectric constants, temperature coefficients at resonant frequency (ppm/°C) and unloaded Q values obtained in such manner are shown in Table 3. In Table 3, those with an asterisk are comparison examples.

As is obvious from the results shown in Table 3, in dielectric ceramic compositions within a composition range of the second aspect of the invention, the dielectric constant is kept at a high value at microwave frequencies, while a high unloaded Q value is provided.

On the contrary, when x is higher than 0.6, the unloaded Q value is significantly reduced as observed in sample Nos. 54 to 56 (Tables 3-2 and 3-3), and 123 (Table 3-6). In addition, when x is below 0.10, the unloaded Q value is reduced as shown in sample Nos. 60, 61 (Table 3-3) and 126 (Table 3-7), and the objects of the invention cannot readily be achieved.

As recognized in sample Nos. 26 to 29 (Table 3-1) and 116 (Table 3-6), since the unloaded Q value is significantly reduced, when y is higher than 0.60, and the unloaded Q value is excessively low, as seen in sample Nos. 15 to 18 (Table 3-1) and 114 (Table 3-6), when y is below 0.20, the objects of the invention cannot readily be achieved.

When z is higher than 0.70, the unloaded Q value is reduced as observed in sample Nos. 30 to 33 (Table 3-1) and No. 117 (Table 3-6); and the temperature coefficient at resonant frequency is excessively high and the unloaded Q value is significantly reduced as in sample No. 36 (Table 3-2) when z is below 0.01, the objects of the invention cannot readily be achieved. Additionally, although the unloaded Q value can be improved by increasing w to a higher value than 0, however, when w exceeds 1.50, the unloaded Q value is reduced as shown in sample Nos. 93 to 96 (Tables 3-4 and 3-5) and 133 (Table 3-7). However, even in the case of sample No. 133, its properties were better than those of conventional dielectric ceramics.

Incidentally, it was confirmed within the composition range of the example that the unloaded Q value was improved by using A, which is at least one element selected from Mg, Co, Zn, Ni and Mn, and Nb oxide that were calcined beforehand at a temperature of 800 to 1200 °C.

Moreover, it was confirmed within the composition range of the example that the degree of sintering was improved by slightly adding an additive, and the properties were not significantly inferior. For example, although the sintering temperature was reduced by approximately 50 °C, when 0.08 wt.% of Al₂O₃ was added to sample No. 105 (Table 3-5), and was reduced by approximately 25 °C, when 0.08 wt.% of SiO₂ was added, the properties were not changed significantly in either case. Moreover, even in the case of dielectric ceramic with 0.1 mol% of at least one compound of BaCO₃, SrCO₃, La₂O₃ and Sm₂O₃ added thereto, the properties were not significantly changed. Other components may be added as far as the objects of the invention are not adversely affected.

Example 3

As initial materials, ZrO₂, TiO₂, MgO, CoO, ZnO, NiO, MnCO₃ and Ta₂O₅ of high chemical purity were used, weighed so as to make a predetermined composition as shown in Table 4 and wet-blended with ethanol by using a ball mill. The volume ratio between the powders and ethanol was approximately 2:3. The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hrs at a temperature of 900 to 1250 °C in the air. The calcination product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powders were mixed with 8% by weight of polyvinyl alcohol solution of 6% in concentration added thereto as a binder, homogenized, and granulated by sieving through 32 mesh screen. The granulated powders were molded into a disk of 7 mm in diameter and approximately 3 mm in thickness by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm². The

molding was placed in a magnesia vessel of high purity, kept in the air at a temperature of 400 to 700 °C for 4 to 8 hrs for removing binders, and succeedingly retained in the air at a temperature of 1300 to 1650 °C for 1 to 100 hrs for sintering, and dielectric ceramics were obtained.

The resonant frequency, unloaded Q (Qu) value and dielectric constant ϵ , were obtained from measurement by the dielectric rod resonator method. The temperature coefficient at resonant frequency τ , was obtained in a range between -25 and 85 °C. The resonant frequency was within a range of 5 to 10 GBz.

The dielectric constants, temperature coefficients at resonant frequency (ppm/°C) and unloaded Q values obtained in such manner are shown in Table 4. In Table 4, those with an asterisk are comparison examples outside the range of the invention.

As obviously recognized from a result shown in Table 4, in dielectric ceramic compositions within a composition range of the third aspect of the invention, the dielectric constant is kept at a high value at microwave frequencies, while providing a high unloaded Q value.

Within the composition range of the invention, when x is higher than 0.60, because the unloaded Q value is significantly reduced as shown in sample No. 152 (Table 4-1), the objects of the invention cannot readily be achieved. Also, when x is below 0.10, since the unloaded Q value is reduced as in sample No. 155 (Table 4-2), the objects of the invention cannot easily be fulfilled.

The unloaded Q value is significantly reduced as seen in sample No. 138 (Table 4-1), when y is higher than 0.60; and the unloaded Q value is too low as in sample No. 134 (Table 4-1), when y is below 0.10 as well, the objects of the invention cannot readily be achieved.

The unloaded Q value is reduced as observed in sample No. 139 (Table 4-1), when z is higher than 0.80; and it is significantly reduced as in sample No. 141 (Table 4-1), when z is lower than 0.01, thus, the objects of the invention cannot readily be achieved.

In addition, although the unloaded Q value can be improved by increasing w to a higher value than 0, the objects of the invention cannot be attained, because the unloaded Q value is significantly reduced, when w is higher than 1.00, as recognized in sample No. 168 (Table 4-2).

Incidentally, it was confirmed within the composition range of the example that the unloaded Q value was superior when powdery oxide of A, which is at least one element selected from Mg, Co, Zn, Ni and Mn, and powdery oxide of Ta calcined beforehand at a temperature of 800 to 1200 °C was used.

Moreover, it was confirmed within the composition range of the invention that the degree of sintering could be enhanced by slightly adding an additive, and the properties were not significantly inferior. For example, although the sintering temperature was reduced by approximately 100 °C when 0.08 wt.% of Al_2O_3 was added to sample No. 151 (Table 4-1); and it was reduced by approximately 50 °C when 0.08 wt.% of SiO_2 was added, the properties were not changed significantly in either case. Furthermore, even in the case of dielectric ceramics with 0.1 mol% of at least one compound of BaCO_3 , SrCO_3 , La_2O_3 and Sm_2O_3 added thereto, the properties were not significantly reduced. Other components may be added as far as the objects of the invention are not adversely affected.

Additionally, a ZrTiO_4 phase or one recognized as being crystallographically a ZrTiO_4 phase was confirmed by powder X-ray diffraction of a dielectric ceramic within the composition range of Examples 1 to 3 of the invention. It was further confirmed in composition analysis by a local X-ray diffractometer of a fracture surface and polished surface of dielectric ceramic having, as the main component, a ZrTiO_4 phase or crystallographically a ZrTiO_4 phase that all components of Zr, Ti, A and B wherein A is at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, and B is at least one component selected from the group (B) consisting of Nb and Ta, were present in a single grain, and their composition ratio was consistent with the composition ratio between other grains that constitute the main phase in the same dielectric ceramic. It was also confirmed that all components A and B blended were present in a single grain. Moreover, it was confirmed that a dielectric ceramic with components Zr, Ti, A and B present in a single grain showed a higher lattice constant in comparison with a ZrTiO_4 ceramic not containing A and B obtained under the same sintering conditions. Accordingly, it was confirmed that components A and B are substituted in the ZrTiO_4 phase or the crystallographically ZrTiO_4 phase.

Such dielectric ceramic specifically showed a high unloaded Q value, high dielectric constant, and was superior in thermo-stability at resonant frequency, and the unloaded Q value was even higher, when the molar fraction ratio of component A to component B was 0.5 or more and 1.0 or less.

It would be appreciated that dielectric ceramics according to the fourth and fifth aspects of the invention are capable of maintaining the dielectric constant at a high value at microwave frequencies, while providing a high unloaded Q value, and are superior in thermo-stability at resonant frequency.

Example 4

As initial materials, ZrO_2 , TiO_2 , MgO , CoO , ZnO , NiO , $MnCO_3$ and Nb_2O_5 of high chemical purity were used, weighed so as to make a predetermined composition as shown in Table 5, and wet-blended with ethanol by using a ball mill. The volume ratio between the powders and ethanol was approximately 2:3. The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hours at a temperature of 900 to 1250 °C in the air. The calcination product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powders were mixed with 10% by weight of polyvinyl alcohol solution of 6% in concentration added thereto as a binder, homogenized, and granulated by sieving them through 32 mesh screen. The granulated powders were molded into cylinders of 16, 35 and 70 mm in diameter by using molds and an oil hydraulic press at a molding pressure of 1 ton/cm². The ratio between diameter and thickness of the molding was arranged to be approximately 2:1. The moldings were placed in a magnesia vessel of high purity, kept in the air at a temperature of 400 to 700 °C for 2 to 100 hrs to remove binders, and then retained in the air at a temperature of 1300 to 1650 °C for 1 to 100 hrs for sintering, and dielectric ceramics were obtained. The dielectric ceramic was placed in the center of a cylindrical cavity made of copper with silver plating (10 μm thick), and a dielectric resonator utilizing TE_{01δ}-mode resonance of the dielectric by electromagnetic wave emitted from an antenna placed in a side surface of the cavity was constructed. The inner dimensions of the cylindrical copper cavity were about four times larger than the diameter and thickness of the dielectric ceramic, respectively, and the thickness was 5 mm. The resonant frequency and Qu value were obtained by measurement with a vector network analyzer. In the case of a molding with a diameter of 16 mm, the resonant frequencies were 2 to 5 GHz, 35 mm, 1 to 2.5 GEz, and 70 mm, 0.6 to 1.5 GHz.

The resonant frequencies (f) and products f×Qu value obtained in such manner are shown in Table 5. In Table 5, those with an asterisk are comparison examples outside the range of the invention.

As evidently seen from a result shown in Table 5, the TE_{01δ}-mode dielectric resonator according to the seventh aspect of the invention has a high unloaded Q value in microwave frequency range and a significantly high unloaded Q value in a relatively low frequency range.

In addition, the volume of dielectric ceramic at resonant frequency of 0.8 GHz is approximately 113 cc in ZrO_2 - SnO_2 - TiO_2 ceramic ($\epsilon_r = 37.0$) and 200 cc in $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic ($\epsilon_r = 24.0$), for example, while the volume of sample No. 177 (Table 5-1) of the invention, for example, is about 83 cc. As the volume of TE_{01δ}-mode dielectric resonator corresponds to that of the dielectric ceramic, the TE_{01δ}-mode dielectric resonator according to the seventh aspect of the invention comes to be significantly compact in a relatively low frequency range. Moreover, since the dielectric ceramic is reduced in size and weight as compared with conventional ones, material and manufacturing costs for such a dielectric resonator are reduced.

Example 5

As initial materials, ZrO_2 , TiO_2 , MgO , CoO , ZnO , NiO , $MnCO_3$ and Ta_2O_5 of high chemical purity were used, weighed so as to make a predetermined composition as shown in Table 6 and wet-blended with ethanol by using a ball mill. The volume ratio between the powders and ethanol was approximately 2:3. The mixture was removed from the ball mill, dried, and calcined for 2 to 8 hours at a temperature of 900 to 1250 °C in the air. The calcination product was wet-milled in the ball mill with ethanol. After the milled slurry was removed from the ball mill and dried, the powders were mixed with 8% by weight of polyvinyl alcohol solution of 6% in concentration added thereto as a binder, homogenized, and granulated by sieving them through 32 mesh screen. The granulated powders were molded into disks of 7, 16, 42 and 70 mm in diameter by using molds and an oil hydraulic press at a molding pressure of 1.3 ton/cm². The ratio between diameter and thickness of the molding was arranged to be approximately 2:1. The moldings were placed in a magnesia vessel of high purity, and kept in the air at a temperature of 1300 to 1650 °C for 1 to 100 hrs for sintering, and dielectric ceramics were obtained. The dielectric ceramic was placed in the center of a cylindrical cavity made of copper with silver plating (10 μm thick), and a dielectric resonator utilizing TE_{01δ}-mode resonance of the dielectric by electromagnetic wave emitted from an antenna placed in a side surface of the cavity was constructed. The inner dimensions of the cylindrical copper cavity were about four times larger than the diameter and thickness of the dielectric ceramic, respectively, and the thickness was 5 mm. The resonant frequency and Qu value were obtained by measurement with a vector network analyzer. In the case of a molding with a diameter of 7 mm, the resonant frequencies were 8 to 9 GHz, 16 mm, 3 to 4 GHz, 42 mm, 1 to 2 GHz, and 70 mm, 0.6 to 0.9 GHz.

The values of the resonant frequencies (f) and products f×Qu obtained in such manner are shown in Table 6. In Table 6, those with an asterisk are comparison examples outside the range of the invention.

As is evident from the results shown in Table 6, the $TE_{0,1\delta}$ -mode dielectric resonator according to the eighth aspect of the invention has a high unloaded Q value in microwave frequency range and a significantly high unloaded Q value in a relatively low frequency range.

In addition the volume of dielectric ceramic at resonant frequency of 0.8 GHz is approximately 113 cc in ZrO_2 - SnO_2 - TiO_2 ceramic ($\epsilon_r = 37.0$), and about 200 cc in $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic ($\epsilon_r = 24.0$), for example, while the volume of sample No. 211 of the invention, for example, is about 98 cc. As the volume of $TE_{0,1\delta}$ -mode dielectric resonator corresponds to that of dielectric ceramic, the $TE_{0,1\delta}$ -mode dielectric resonator according to the eighth aspect of the invention comes to be significantly compact in a relatively low frequency range. Moreover, since the dielectric ceramic is reduced in size and weight as compared with conventional ones, the material and manufacturing costs of such a dielectric resonator are reduced.

Although a dielectric ceramic of cylindrical shape is used in Examples 4 and 5, it is not limited to such shape, and it was confirmed by the inventors that the $TE_{0,1\delta}$ -mode dielectric resonator having an equivalent or higher unloaded Q value can be constructed by using, for example, an annular dielectric ceramic as well.

As shown in Example 1, because a dielectric ceramic having, as the main component, a complex oxide formed of Zr, Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta reduces variation of temperature coefficient at resonant frequency due to the heating history during sintering of $ZrTiO_4$ and ZrO_2 - SnO_2 - TiO_2 ceramics, the $TE_{0,1\delta}$ -mode dielectric resonator comprising such dielectric ceramic, that is, the $TE_{0,1\delta}$ -mode dielectric resonator according to the sixth aspect of the invention is useful.

Also, the existence of the $ZrTiO_4$ phase or crystallographically $ZrTiO_4$ phase was confirmed by powder X-ray diffraction in the dielectric ceramics of Examples 1 to 5 of the invention. Moreover, it was confirmed in composition analysis by a local X-ray diffractometer of a fracture surface and polished surface of dielectric ceramic having, as the main component, $ZrTiO_4$ phase or crystallographically $ZrTiO_4$ phase that all components Zr, Ti, A and B, wherein A is at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn, and B is at least one component selected from the group (B) consisting of Nb and Ta, were present in a single grain, and their composition ratio agreed with that of other grains that constitute the main phase in the same dielectric ceramic. It was also confirmed that all components A and B blended were present in a single grain. It was further confirmed that a dielectric ceramic with components Zr, Ti, A and B present in a single grain showed a higher lattice constant in comparison with $ZrTiO_4$ ceramic obtained in the same sintering condition. Accordingly, it was confirmed that components A and B are substituted in the $ZrTiO_4$ phase or crystallographically $ZrTiO_4$ phase.

Such dielectric ceramic specifically showed a high unloaded Q value and high dielectric constant, and was superior in thermo-stability at resonant frequency, and the unloaded Q value was even higher, when the A:B molar fraction ratio was 0.5 or more and 1.0 or less. In other words, the $TE_{0,1\delta}$ -mode dielectric resonators according to the ninth and tenth aspects of the invention have a high unloaded Q value, while maintaining the dielectric constant at a high value at microwave frequencies, and are superior in thermo-stability at resonant frequency.

Especially, in the dielectric ceramic compositions according to the invention, above all sample Nos. 43 to 53, 62 to 92, 97 to 113 and 112 are specifically superior as compositions in which the dielectric constant and unloaded Q value are high, the temperature coefficient at resonant frequency is low, and niobium which is less expensive than tantalum is used. In addition, as dielectric resonators, sample Nos. 117, 180, 183, 186 to 188, 194 and 195 are particularly superior in such aspect that niobium which costs less than tantalum is used.

According to the dielectric ceramic of the invention, variation of temperature coefficient at resonant frequency due to heat history during sintering of $ZrTiO_4$ and ZrO_2 - SnO_2 - TiO_2 ceramics can be reduced, a high unloaded Q value is provided, and the temperature coefficient at resonant frequency can be changed as desired without reducing the dielectric constant. In other words, a dielectric ceramic having the temperature coefficient of desired value can be obtained by changing the content of the components of dielectric ceramic composition.

Furthermore, according to the structure of the $TE_{0,1\delta}$ -mode dielectric resonator of the invention, a dielectric resonator having a high unloaded Q value in a frequency range of 0.8 to 5 GHz with a compact size can be achieved.

TABLE 1

Sample NO	Composition (molar fraction)									
	Zr	Ti	Mg	Co	Zn	Ni	Mn	Nb	Ta	Sn
*1,*2	0.50	0.50	0	0	0	0	0	0	0	0
3,4	0.35	0.50	0.05	0	0	0	0	0.10	0	0
5,6	0.35	0.50	0	0.05	0	0	0	0.10	0	0
7,8	0.35	0.50	0.01	0.01	0.01	0.01	0.01	0.10	0	0
9,10	0.35	0.50	0.01	0.01	0.01	0.01	0.01	0.05	0.05	0
*11,*12	0.40	0.50	0	0	0	0	0	0	0	0.10
*13,*14	0.32	0.50	0	0.03	0	0	0	0.05	0	0.10

TABLE 2

Sample No.	Cooling condition after sintering	τ_1 (ppm/°C)
*1	Quenching	53.7
*2	Slow cooling	64.3
3	Quenching	3.5
4	Slow cooling	3.8
5	Quenching	5.2
6	Slow cooling	3.9
7	Quenching	4.9
8	Slow cooling	4.8
9	Quenching	0.5
10	Slow cooling	0.9
*11	Quenching	-8.7
*12	Slow cooling	1.2
*13	Quenching	-24.5
*14	Slow cooling	-16.3

TABLE 3-1

Sample no.	A	Composition (molar fraction) (Value)				ϵ_r	τ_f	Q_u
		x	y	z	w			
*15	Mg	0.400	0.150	0.450	0	30.2	-85.2	950
*16	Co	0.400	0.150	0.450	0	29.8	-70.5	850
*17	Zn	0.400	0.150	0.450	0	30.0	-88.6	980
*18	Ni	0.400	0.150	0.450	0	30.5	-69.5	850
19	Mg	0.200	0.200	0.600	0	30.0	-48.5	9000
20	Co	0.200	0.200	0.600	0	28.6	-35.6	9300
21	Ni	0.200	0.200	0.600	0	28.0	-30.8	8200
22	Mg	0.450	0.200	0.350	0	31.8	-50.0	5200
23	Co	0.450	0.200	0.350	0	32.6	-28.9	5700
24	Mg	0.200	0.600	0.200	0	57.5	47.5	5500
25	Zn	0.200	0.600	0.200	0	55.5	40.0	6200
26	Mg	0.150	0.700	0.150	0	74.5	189.5	520
27	Co	0.150	0.700	0.150	0	98.8	255.6	210
28	Zn	0.150	0.700	0.150	0	71.5	162.6	630
29	Ni	0.150	0.700	0.150	0	75.5	320.6	190
30	Mg	0.150	0.120	0.730	0	28.0	-85.0	1200
31	Co	0.150	0.120	0.730	0	24.5	-65.8	1000
32	Zn	0.150	0.120	0.730	0	26.9	-88.9	800
33	Ni	0.150	0.120	0.730	0	23.6	-56.7	900
34	Mg	0.100	0.200	0.700	0	33.8	-8.5	9800

TABLE 3-2

Sample No.	A	Composition (molar fraction) (Value)				ϵ_r	τ_f	Q_u
		x	y	z	w			
35	Ni	0.100	0.200	0.700	0	26.8	-5.6	9500
*36		0.550	0.450	0	0	45.8	250.8	1800
37	Mg	0.490	0.500	0.010	0	44.5	42.5	3800
38	Co	0.490	0.500	0.010	0	44.3	42.0	3600
39	Zn	0.490	0.500	0.010	0	43.8	45.9	3300
40	Ni	0.490	0.500	0.010	0	44.5	46.5	3400
41	Mg	0.300	0.300	0.400	0	37.5	-32.0	7000
42	Co	0.300	0.300	0.400	0	38.6	-20.3	5600
43	Mg	0.400	0.400	0.200	0	42.0	0	9600
44	Co	0.400	0.400	0.200	0	43.2	12.6	8500
45	Zn	0.400	0.400	0.200	0	42.0	-5.9	8900
46	Mg	0.340	0.520	0.140	0	42.6	5.5	7500
47	Co	0.340	0.520	0.140	0	44.3	8.3	5600
48	Zn	0.340	0.520	0.140	0	42.9	-3.6	7400
49	Ni	0.340	0.520	0.140	0	42.4	13.9	4800
50	Mg	0.450	0.450	0.100	0	41.0	6.5	5200
51	Co	0.450	0.450	0.100	0	42.6	9.8	4900
52	Mg	0.400	0.500	0.100	0	41.4	-1.2	8600
53	Co	0.400	0.500	0.100	0	43.5	-3.6	9300
*54	Mg	0.650	0.200	0.100	0	35.8	59.7	1400

TABLE 3-3

Sample no.	A	Composition (molar fraction) (Value)				ϵ_r	τ_i	Q_u
		x	y	z	w			
55	Co	0.650	0.200	0.100	0	29.6	21.3	580
56	Zn	0.650	0.200	0.100	0	23.2	36.5	860
57	Mg	0.600	0.300	0.100	0	40.2	45.7	4800
58	Mg	0.100	0.400	0.500	0	64.5	49.8	4000
59	Ni	0.100	0.400	0.500	0	53.6	48.6	4500
60	Mg	0.050	0.500	0.450	0	82.9	153.2	980
61	Co	0.050	0.500	0.450	0	86.9	213.5	230
62	Mg	0.450	0.350	0.200	0	41.5	-9.8	4900
63	Zn	0.450	0.350	0.200	0	41.3	-21.3	5200
64	Ni	0.450	0.350	0.200	0	42.5	-3.9	4900
65	Mg	0.350	0.450	0.200	0	43.5	12.5	6000
66	Co	0.350	0.450	0.200	0	45.6	26.9	5100
67	Zn	0.350	0.450	0.200	0	42.5	3.6	5800
68	Ni	0.350	0.450	0.200	0	42.9	30.6	4800
69	Mg	0.350	0.450	0.200	0.01	43.5	12.4	6350
70	Co	0.350	0.450	0.200	0.01	45.5	26.5	5300
71	Zn	0.350	0.450	0.200	0.01	42.6	3.6	5900
72	Ni	0.350	0.450	0.200	0.01	42.9	30.6	5100
73	Mg	0.350	0.450	0.200	0.05	43.1	10.8	6700
74	Co	0.350	0.450	0.200	0.05	45.1	22.6	5600

TABLE 3-4

Sample No.	A	Composition (molar fraction) (Value)				ϵ_r	τ_i	Q_u
		x	y	z	w			
75	Zn	0.350	0.450	0.200	0.05	41.9	2.8	6200
76	Ni	0.350	0.450	0.200	0.05	41.6	25.8	5500
77	Mg	0.350	0.450	0.200	0.20	42.6	7.5	6800
78	Co	0.350	0.450	0.200	0.20	44.0	20.3	5900
79	Zn	0.350	0.450	0.200	0.20	40.3	1.8	6500
80	Ni	0.350	0.450	0.200	0.20	41.2	18.6	5700
81	Mg	0.350	0.450	0.200	0.50	42.3	1.2	8020
82	Co	0.350	0.450	0.200	0.50	42.3	11.9	6300
83	Zn	0.350	0.450	0.200	0.50	38.0	-1.3	6600
84	Ni	0.350	0.450	0.200	0.50	40.2	13.5	5900
85	Mg	0.350	0.450	0.200	1.00	39.8	-3.5	7200
86	Co	0.350	0.450	0.200	1.00	39.0	5.3	7100
87	Zn	0.350	0.450	0.200	1.00	35.0	-5.8	7300
88	Ni	0.350	0.450	0.200	1.00	36.7	4.8	6300
89	Mg	0.350	0.450	0.200	1.50	37.4	-6.8	6400
90	Co	0.350	0.450	0.200	1.50	36.5	3.2	6900
91	Zn	0.350	0.450	0.200	1.50	32.1	-9.8	7200
92	Ni	0.350	0.450	0.200	1.50	32.6	0.9	6000
93	Mg	0.350	0.450	0.200	1.80	33.5	-12.2	1350
94	Co	0.350	0.450	0.200	1.80	32.6	-5.6	1200

TABLE 3-5

Sample No.	A	Composition (molar fraction) (Value)				ϵ_r	τ_i	Q_u
		x	y	z	w			
*95	Zn	0.350	0.450	0.200	1.80	29.6	-15.6	1400
*96	Ni	0.350	0.450	0.200	1.80	29.6	-5.9	850
97	Mg _{1/2} Co _{1/2}	0.340	0.520	0.140	0	43.8	6.1	6900
98	Mg _{2/3} Co _{1/3}	0.340	0.520	0.140	0	43.4	5.7	7200
99	Mg _{1/2} Zn _{1/2}	0.340	0.520	0.140	0	42.8	0.5	7200
100	Mg _{1/3} Co _{1/3} Ni _{1/3}	0.340	0.520	0.140	0	42.9	8.5	6900
101	Mg _{1/4} Co _{1/4} Zn _{1/4} Ni _{1/4}	0.340	0.520	0.140	0	43.0	12.0	5900
102	Mg _{1/2} Co _{1/2}	0.340	0.520	0.140	1.00	43.2	2.6	7100
103	Mg _{1/3} Co _{1/3} Ni _{1/3}	0.340	0.520	0.140	1.00	40.5	5.2	7600
104	Mg _{1/4} Co _{1/4} Zn _{1/4} Ni _{1/4}	0.340	0.520	0.140	1.00	41.2	2.6	6800
105	Mg _{39/40} Mn _{1/40}	0.340	0.520	0.140	0.02	42.7	5.4	8500
106	Mg _{443/500} Mn _{57/500}	0.338	0.517	0.145	0.08	42.6	5.4	8300
107	Mg _{361/500} Mn _{139/500}	0.334	0.511	0.155	0.23	42.5	5.3	8200
108	Mg _{113/200} Mn _{87/200}	0.328	0.502	0.170	0.41	42.4	5.1	7900

TABLE 3-6

Sample No.	A	Composition (molar fraction) (Value)				ϵ_r	τ_i	Q_u
		x	y	z	w			
109	Co _{487/500} Mn _{13/500}	0.340	0.519	0.141	0.02	44.2	8.1	6400
110	Zn _{487/500} Mn _{13/500}	0.340	0.519	0.141	0.02	42.5	-3.5	8100
111	Ni _{487/500} Mn _{13/500}	0.340	0.519	0.141	0.02	42.3	9.8	6200
112	Mg _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	39.8	-3.8	7600
113	Co _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	39.2	5.0	7500
*114	Mn	0.400	0.050	0.550	0	27.5	-50.2	320
115	Mn	0.200	0.600	0.200	0	60.4	49.5	3200
*116	Mn	0.150	0.700	0.150	0	78.3	210.9	280
*117	Mn	0.100	0.080	0.820	0	20.9	-52.3	1200
118	Mn	0.490	0.500	0.010	0	44.7	44.5	3500
119	Mn	0.350	0.350	0.300	0	34.8	-23.8	4800
120	Mn	0.400	0.400	0.200	0	37.3	-9.8	4700
121	Mn	0.300	0.500	0.200	0	46.4	20.5	4500
122	Mn	0.400	0.500	0.100	0	43.8	0.9	6300
*123	Mn	0.650	0.250	0.100	0	30.4	-15.6	360
124	Mn	0.600	0.300	0.100	0	33.1	4.3	4500

TABLE 3-7

Sample No.	A	Composition (molar fraction) (Value)				ϵ_r	τ_f	Q_u
		x	y	z	w			
125	Mn	0.100	0.400	0.500	0	48.7	48.6	3600
*126	Mn	0.050	0.450	0.500	0	75.2	183.2	240
127	Mn	0.450	0.350	0.200	0	35.5	-15.6	3900
128	Mn	0.330	0.470	0.200	0	43.5	3.5	5300
129	Mn	0.330	0.470	0.200	0.01	43.5	3.5	5500
130	Mn	0.330	0.470	0.200	0.10	43.5	3.4	5500
131	Mn	0.330	0.470	0.200	0.50	43.8	3.9	5800
132	Mn	0.330	0.470	0.200	1.00	43.9	3.9	6000
133	Mn	0.330	0.470	0.200	2.00	45.1	5.2	5000

TABLE 4-1

Sample No.	A	Composition (molar fraction) (Value)				ϵ_r	τ_f	Q_u
		x	y	z	w			
*134	Mg	0.400	0.050	0.550	0	29.8	-77.5	950
135	Mg	0.300	0.100	0.600	0	31.0	-48.5	7500
136	Mg	0.500	0.100	0.400	0	30.2	-43.5	6400
137	Mg	0.200	0.600	0.200	0	58.9	48.2	4100
*138	Mg	0.150	0.700	0.150	0	70.3	177.9	680
*139	Mg	0.100	0.080	0.820	0	27.9	-56.3	1000
140	Mg	0.100	0.100	0.800	0	31.5	-12.5	13500
*141		0.550	0.450	0	0	45.8	250.8	1800
142	Mg	0.490	0.500	0.010	0	44.8	45.5	3900
143	Mg	0.350	0.350	0.300	0	36.1	-26.5	7800
144	Mg	0.400	0.400	0.200	0	38.8	-14.8	6700
145	Mg	0.300	0.500	0.200	0	45.5	16.1	8200
146	Mg	0.400	0.500	0.100	0	42.5	0	8600
147	Co	0.400	0.500	0.100	0	43.5	3.5	8200
148	Zn	0.400	0.500	0.100	0	43.5	-3.5	7900
149	Ni	0.400	0.500	0.100	0	40.9	1.0	7600
150	Mn	0.400	0.500	0.100	0	43.8	4.5	6900
151	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.400	0.500	0.100	0	42.9	0.7	8900
*152	Mg	0.650	0.250	0.100	0	32.3	-4.5	950
153	Mg	0.600	0.300	0.100	0	40.1	5.5	4500

TABLE 4-2

Sample No.	A	Composition (molar fraction) (Value)				ϵ	τ	ρ_s
		x	y	z	w			
154	Mg	0.100	0.400	0.500	0	62.8	49.8	3600
*155	Mg	0.050	0.450	0.500	0	73.4	135.0	780
156	Mg	0.450	0.350	0.200	0	41.5	-9.8	4900
157	Mg	0.330	0.470	0.200	0	42.1	-1.0	8700
158	Mg	0.330	0.470	0.200	0.01	42.1	-0.8	8800
159	Mg	0.330	0.470	0.200	0.05	41.8	-0.5	8950
160	Mg	0.330	0.470	0.200	0.20	41.0	0	9200
161	Co	0.330	0.470	0.200	0.20	40.5	4.6	8900
162	Zn	0.330	0.470	0.200	0.20	40.2	-1.3	8700
163	Ni	0.330	0.470	0.200	0.20	38.4	6.0	7300
164	Mn	0.330	0.470	0.200	0.20	42.9	3.5	6300
165	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.330	0.470	0.200	0.20	41.8	0.9	9500
166	Mg	0.330	0.470	0.200	0.50	40.0	1.2	9830
167	Mg	0.330	0.470	0.200	1.00	37.8	4.5	9950
*168	Mg	0.330	0.470	0.200	1.10	32.1	8.9	1800

TABLE 5-1

Sample No.	A	Composition (molar fraction) (Value)				f (G)	fQu (G)
		x	y	z	w		
*169		0.410	0.590	0	0	3.82	40000
*170		0.410	0.590	0	0	1.65	25000
*171		0.410	0.590	0	0	0.79	8500
172	Mg	0.340	0.520	0.140	0	3.85	58500
173	Mg	0.340	0.520	0.140	0	1.69	51000
174	Mg	0.340	0.520	0.140	0	0.80	35300
175	Mg _{39/40} Mn _{1/40}	0.340	0.520	0.140	0.02	3.84	60200
176	Mg _{39/40} Mn _{1/40}	0.340	0.520	0.140	0.02	1.68	56100
177	Mg _{39/40} Mn _{1/40}	0.340	0.520	0.140	0.02	0.81	48700
178	Mg	0.350	0.450	0.200	1.00	3.95	60000
179	Mg	0.350	0.450	0.200	1.00	1.72	54200
180	Mg	0.350	0.450	0.200	1.00	0.90	46300
181	Mg _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	3.94	60000
182	Mg _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	1.72	56800
183	Mg _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	0.91	52500

TABLE 5-2

Sample No.	A	Composition (molar fraction) (Value)				f (G)	fQu (G)
		x	y	z	w		
184	Co _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	3.90	56000
185	Co _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	1.69	51200
186	Co _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	0.87	47200
187	Zn _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	0.88	46500
188	Ni _{1983/2000} Mn _{17/2000}	0.350	0.449	0.201	1.01	0.85	48000
189	Mn	0.400	0.500	0.100	0	3.83	51000
190	Mn	0.400	0.500	0.100	0	1.62	45000
191	Mn	0.400	0.500	0.100	0	0.79	35200
192	Mn	0.400	0.500	0.100	1.00	3.81	54100
193	Mn	0.400	0.500	0.100	1.00	1.62	45300
194	Mn	0.400	0.500	0.100	1.00	0.76	38100
195	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.400	0.500	0.100	0	0.79	54200

TABLE 6

Sample No.	A	Composition (molar fraction) (Value)				SnO ₂ molar %	f (G)	fQu (G)
		x	y	z	w			
*196		0.400	0.500	0	0	0.10	9.002	55000
*197		0.400	0.500	0	0	0.10	4.036	27100
*198		0.400	0.500	0	0	0.10	1.524	15300
199		0.400	0.500	0	0	0.10	0.900	10200
200	Mg	0.330	0.470	0.200	0	0	8.519	74100
201	Mg	0.330	0.470	0.200	0	0	3.884	51800
202	Mg	0.330	0.470	0.200	0	0	1.502	28100
203	Mg	0.330	0.470	0.200	0	0	0.788	25400
204	Mg	0.330	0.470	0.200	0.20	0	8.598	76200
205	Mg	0.330	0.470	0.200	0.20	0	3.942	57200
206	Mg	0.330	0.470	0.200	0.20	0	1.511	31500
207	Mg	0.330	0.470	0.200	0.20	0	0.812	26900
208	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.330	0.470	0.200	0.20	0	8.622	81900
209	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.330	0.470	0.200	0.20	0	4.098	63500
210	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.330	0.470	0.200	0.20	0	1.763	56200
211	Mg _{1/5} Co _{1/5} Zn _{1/5} Ni _{1/5} Mn _{1/5}	0.330	0.470	0.200	0.20	0	0.903	48100

Claims

1. A dielectric ceramic comprising as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.
2. A dielectric ceramic composition expressed by Formula (a):

$$x\text{ZrO}_2 - y\text{TiO}_2 - z\text{A}_{(1+w)/3}\text{Nb}_{(2-w)/3}\text{O}_2$$
 Formula (a)

wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.20 to 0.60 and 0.01 to 0.70,

respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula (α)}$$

5 and w denotes a value of 0 to 1.50.

3. A dielectric ceramic composition expressed by Formula (b):



10 wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.10 to 0.60 and 0.01 to 0.80, respectively, and have the relation represented by Formula (α):

$$15 \quad x + y + z = 1 \quad \text{Formula (α)}$$

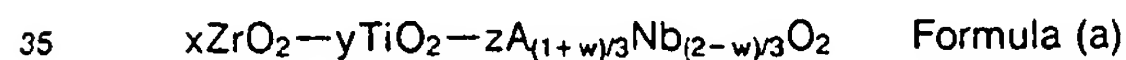
and w denotes a value of 0 to 1.00.

20 4. A dielectric ceramic according to claim 1, wherein the main component comprises a ZrTiO_4 phase substituted with at least one component of group (A) and at least one component of group (B), or the main component crystallographically comprises a ZrTiO_4 phase substituted with at least one component of group (A) and at least one component of group (B).

25 5. A dielectric ceramic according to claim 1 or 4, wherein a molar fraction ratio of the total amount of group (A) to the total amount group (B) ranges from 0.5 to 1.0.

30 6. A $\text{TE}_{01\delta}$ -mode dielectric resonator in which using a dielectric ceramic which mainly comprises a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn and at least one component selected from the group (B) consisting of Nb and Ta.

7. A $\text{TE}_{01\delta}$ -mode dielectric resonator in which using a dielectric ceramic expressed by Formula (a):



wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

40 x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.20 to 0.60 and 0.01 to 0.70, respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula (α)}$$

and w denotes a value of 0 to 1.50.

45 8. A $\text{TE}_{01\delta}$ -mode dielectric resonator in which using a dielectric ceramic expressed by Formula (b):



50 wherein A denotes at least one component selected from the group (A) consisting of Mg, Co, Zn, Ni and Mn,

x, y and z denote molar fractions ranging from 0.10 to 0.60, 0.10 to 0.60 and 0.01 to 0.80, respectively, and have the relation represented by Formula (α):

$$55 \quad x + y + z = 1 \quad \text{Formula (α)}$$

and w denotes a value of 0 to 1.00.

9. A $TE_{0, \delta}$ -mode dielectric resonator according to claim 6, wherein the main component comprises a $ZrTiO_4$ phase substituted with at least one component of group (A) and at least one component of group (B), or the main component crystallographically comprises a $ZrTiO_4$ phase substituted with at least one component of group (A) and at least one component of group (B).

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10. A $TE_{0, \delta}$ -mode dielectric resonator according to claim 6 or 9, wherein a molar fraction ratio of the total amount of group (A) components to the total amounts of group (B) components ranges from 0.5 to 1.0.

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(71) Applicant: MATSUSHITA ELECTRONICS
CORPORATION
1006, Ohaza Kadoma
Kadoma-shi,
Osaka 571 (JP)

(72) Inventor: Okuyama, Kojiro
2-6-1, Inaba Nishi,
Ikaruga-cho
Ikoma-gun,
Nara, 636-01 (JP)
Inventor: Yokotani, Yoichiro
8-C-508, Satsukigaoka higashi
Suita-shi,
Osaka, 565 (JP)
Inventor: Kugimiya, Koichi
2-1-32, Chokoji minami
Toyonaka-shi,
Osaka, 560 (JP)

(74) Representative: VOSSIUS & PARTNER
Postfach 86 07 67
D-81634 München (DE)

(54) Dielectric ceramic compositions and dielectric resonators.

(57) The invention provides a dielectric ceramic including as the main component a complex oxide formed of both Zr and Ti, at least one component selected from the group (A) consisting of {Mg, Co, Zn, Ni and Mn} and at least one component selected from the group (B) consisting of {Nb and Ta} and a TE_{0,δ}-mode dielectric resonator including the dielectric ceramic, and also the invention provides a dielectric ceramic composition expressed by Formula (a):



wherein A denotes at least one component selected from the group (A) consisting of {Mg, Co, Zn, Ni and Mn},

x, y and z denote molar fractions ranging from

0.10 to 0.60, 0.20 to 0.60 and 0.01 to 0.70, respectively, and have the relation represented by Formula (α):

$$x + y + z = 1 \quad \text{Formula (α)}$$

and w denotes a value of 0 to 1.50, and a TE_{0,δ}-mode dielectric resonator in which using the dielectric ceramic.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 11 4417

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-5 132 258 (SANYO ELECTRIC CO., LTD.) * column 2, line 37 - column 3, line 51; claims 1,2; tables 1,2 * ---	1,4-6,9, 10	C04B35/46 C04B35/49
X	EP-A-0 375 518 (COMPAGNIE EUROPEENNE DE COMPOSANTS ELECTRONIQUES LCC) * claim 1; examples 8,9; tables 8,9 * ---	1,4-6,9, 10	
X	FR-A-2 581 639 (MURATA MANUFACTURING CO., LTD.) * example 1; tables 1,2 * ---	1,4-6,9, 10	
X	DE-A-39 15 339 (SAKAI CHEMICAL INDUSTRY CO., LTD.) * claims 1-4; examples 1-5; tables 1-5 * -----	1,4-6,9, 10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C04B C01G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 December 1994	Examiner Luethe, H
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